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Supercritical Fluid Technology in the Oil Processing and Conversion Industry

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In the last decade there has been considerable diversification in applying supercritical fluid technology for other purposes than commodity oilseed extraction. In this presentation we will emphasis developments in three distinct areas: (1) enrichment of high value oil-derived chemicals from seed feedstocks, (2) integrating supercritical fluid-based operations for "green" processing and synthesis of oleochemicals, and (3) the analytical use of supercritical technology for the routine monitoring of oilseed quality. We will cite several examples of enrichment schemes that have been studied at NCAUR, including the enrichment of tocopherols from soybean oil, isolation of phospholipid fractions from deoiled seed meals and fractionation of glyceride mixtures using a thermal gradient column operated under supercritical fluid conditions. The role of reaction chemistry in supercritical media will also be discussed, including enzyme- catalyzed transformations in SC-CO₂, carbon dioxide's role in glycerolysis, and the potential of hydrogenating oils in the presence of supercritical fluid media. Products that have been synthesized include fatty acid methyl esters (FAME), emulsifiers, and potential margarine basestocks. The potential for coupling super- and subcritical processing in various combinations will also be noted. Examples include glycerolysis reactions initiated in the presence of SC-CO₂, followed by packed column fractionation of the resultant glyceride mixture. Similarly, it has been shown that the hydrolysis of vegetable oils to produce fatty acid mixtures of industrial value is feasible under subcritical water conditions. Finally, the routine use of supercritical fluid extraction (SFE) for the determination of oil levels in seed moieties has become an official method of the AOCS/AOAC. Our role in facilitating the acceptance of this methodology will be described, including on-going studies using an enzyme-based reactions that permits the analysis of speciated fat components, according to the Nutritional Labeling & Education Act definition of fat or oil content.

Historical Perspective

The initial interface of supercritical fluid technology with the vegetable oil processing industry occurred in the early 1980's when the technology was examined as an alternative to conventional solvent extraction of commodity oils (Friedrich and List, 1982; Stahl, et al.,

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1988). Despite the promise of the new technology, the oilseeds industry was reluctant to incorporate this environmentally benign extraction of seed oils based on capitalization costs, the need for a truly continuous process that duplicated current liquid extraction technique, and historical reluctance to accept alternative processing technologies. Supercritical carbon dioxide-extracted oils were shown to be superior to liquid-extracted oils in color, gum content, and flavor properties; but also showed a greater propensity toward oxidation because of their depleted phospholipid content. Eggers (1985) however demonstrated that seed oils could be continuously deoiling at supercritical conditions, and to date, no definitive study has appeared which represents accurately the economics of the process (see Reverchon and Osseo, 1994).

Despite the reservations shown towards supercritical fluid extraction (SFE) by the commodity seed oil processing industry, there are cited examples of SFE being effectively applied for extracting speciality oils. An excellent tome which discussed the present status and breath of supercritical fluid technology in oil and lipid chemistry has been rendered by King and List (1996). Perhaps unappreciated by the oilseed industry are the other available options for using sub- and supercritical fluid processing for extracting, refining, reacting, and fractionating lipid-based materials. For example, List, et al. (1993) have shown that solvent-extracted vegetable oils can be effectively degummed and refined to a state that permits the processed oil to be directly subjected to deodorization after supercritical refining. This alternative approach to producing high quality vegetable oils removes the need for degumming after the extraction step, as well as the need for bleaching earths prior to the final deodorization step. This process is a continuous countercurrent refining process with the supercritical carbon dioxide (SC-CO₂) contacting the oil in a high pressure vessel containing Goodloe packing. Lecithin-enriched concentrates can be collected by venting out the bottom of the vessel. A schematic of the processing system is shown in Figure 1.

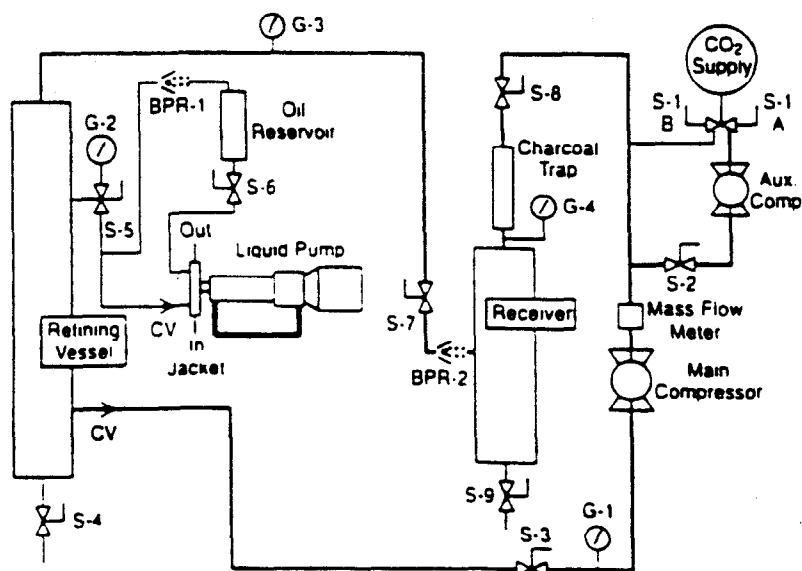


Fig. 1. Schematic of Continuous Supercritical CO₂ - Degumming Equipment. Legend: G, pressure gauge; BPR, back pressure regulator; CV, check valve; S, on/off valve.

In this paper, we shall show adaptability the supercritical fluid-based processing for the enrichment of high-value phytochemicals from seed oil feedstocks and for conducting reactions to convert seed oils to higher value oleochemical derivatives, as well as the exploitation of SC-CO₂ as an extraction/reaction medium in the analytical characterization of seed oils. These processes can be advantageously coupled together to offer some unique "green" processing opportunities as noted by King, et al. (1997a) and depicted in Figure 2. Here naturally-derived products can be altered by supercritical fluid-based processing, not only by SFE, but by coupling supercritical fluid fractionation (SFF), or supercritical fluid reaction (SFR) with the basic SFE isolation step, to produce a plethora of products or fractions.

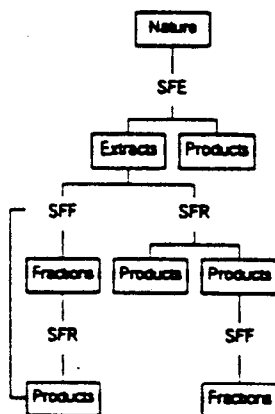


Fig. 2. Process Sequences Utilizing Supercritical Fluid Media for Isolating or Synthesizing Desired End Products

Supercritical fluid research at the National Center for Agricultural Utilization Research (NCAUR) involves a synergistic interaction between process development and analytical chemistry; often times yielding unexpected benefits across interdisciplinary lines. This will be illustrated using examples of phytochemical enrichment and enzyme-catalyzed reactions in both of the above-mentioned disciplines.

Oleochemical-Based Reaction Chemistry in Sub- and Supercritical Fluids

Supercritical fluid media have been receiving increased attention in reaction chemistry, since they can be substituted for conventional liquid solvents yielding a "green" synthetic process (Anastas and Williamson, 1996). Aside from their thermodynamic-based solvent properties, supercritical fluids offer enhanced conditions for favorable mass transport of reactants to catalyst surfaces, and can be coupled with the extraction mode to provide additional versatility to the oleochemical processor. These factors coupled with the potential acceleration of reaction rates at higher pressures and the ability to fractionate the synthesized products via pressure reduction, make supercritical fluids an attractive medium for reaction chemistry.

In some cases, SC-CO₂ can act as a reactant in a process or alternatively as a catalyst.

An example of the latter case is the effect of SC-CO₂ on conversion of vegetable oils to yield mixed glyceride compositions enriched in monoglyceride content. Temelli, et al. (1996) have shown that by subjecting a glycerolysis reaction to a pressure of 21 MPa at 250°C that mixtures of mono-, di- and triglycerides, equivalent to those obtained using alkali metal catalysts, can be synthesized. However absence of the metal catalysts in the SC-CO₂ initiated process eliminates the troublesome filtration step associated with the currently used industrial process. Further, the produced mixed glyceride compositions are much lighter in color than those synthesized using metal catalysts. These end products are the low cost end of the glyceride-based emulsifier market, and as will be shown later, can be enriched to a higher monoglyceride content via supercritical fluid fractionation.

Another area of activity at NCAUR is the use of enzyme-catalyzed conversion of lipids in the presence of SC-CO₂/cosolvent mixtures. Our studies to date have centered on the use of Novozym SP 435 (Novo Nordisk, Franklinton, NC) as a multi-functional enzymatic catalyst for performing esterifications, acylations, transesterifications, glycerolysis and interesterifications (see Figure 3). Under appropriate conditions; temperatures less than 70°C and pressures in the interval of 17-41 MPa, the above conversions can be successfully achieved. Initial research by Jackson and King (1996) demonstrated that vegetable oils could be readily converted to their methyl esters after SFE of the seed moiety via transesterification over the supported Novozym SP 435 catalyst in the presence of flowing SC-CO₂ containing dissolved methanol. The synthesized methyl esters were identical in composition to those obtained by alkali metal initiated methanolysis. Again the advantage of the supercritical fluid synthesis becomes apparent since it eliminates catalyst filtration after completion of the reaction. The highly reproducible quantitative conversion of soybean and corn oils to their methyl esters via the enzymatic-catalyzed reaction in flowing SC-CO₂ suggested to us that the reaction might have some analytical utility which will be demonstrated later in the text.

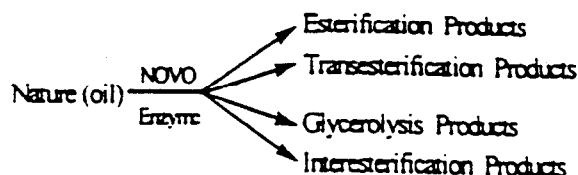


Fig. 3. Transformations of Natural Oils via Enzymatic Catalysis in SC-CO₂.

Further exploration by King and Jackson (1997) showed that under the same experimental conditions, the Novozym SP 435 catalyst could initiate glycerolysis of vegetable oils to yield monoglyceride-containing mixtures varying in composition depending on the reaction conditions. Key parameters in controlling the resultant monoglyceride concentration in the end product were the water content of the polyol participating in the reaction, the flow rate of the reactants, and supercritical fluid. Monoglyceride compositions approaching 90 wt. % can be achieved by this method. Surprisingly the reaction appears to take place in a multi phase system since typical polyol compositions exceed their equilibrium solubility levels in SC-CO₂. This invention is the subject of a U.S. patent application (Jackson, 1996) that has recently been granted.

Along a similar theme, Jackson, et al. (1997) demonstrated that the above lipase could also effectively randomize vegetable oils to yield potential products for incorporation into margarine formulations. The degree of randomization attained on the vegetable oils dissolved in SC-CO₂ was a function of extraction/reaction pressure, the flow rate of the SC-CO₂, and the quantity of enzyme utilized. Dropping point and solid fat index (SFI) data of the products randomized in SC-CO₂ were compared to oils randomized by conventional methods, and the agreement between these two differently synthesized products was encouraging. As shown in Figure 4, randomized palm olein (PO) and a genetically-engineered soybean oil randomized in SC-CO₂ (HS-1) had similar SFI as a function of temperature to hydrogenated blends of vegetable oils. This illustrates how a customized oleochemical-derived product can be synthesized using a reaction conducted in supercritical fluid media.

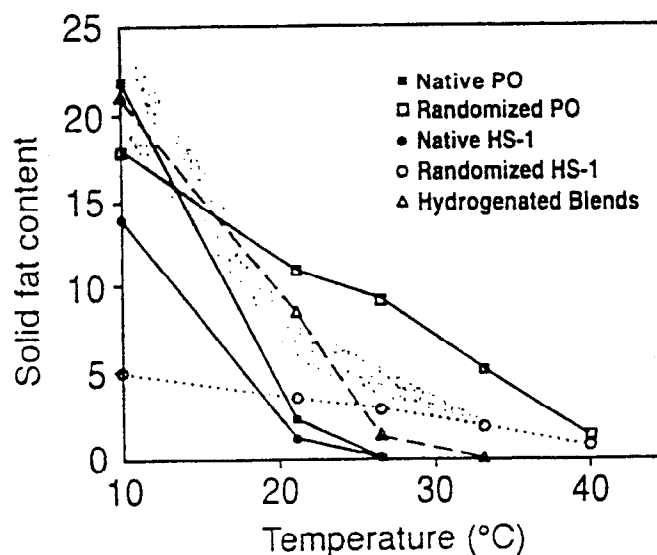


Fig. 4. Solid Fat Content of Palm Olein (PO) and HS-1 Soybean Oil (Jacob Hartz Seed Co., Stuttgart, AR) Before and After Randomization.

Another synthetic option we have explored is using heated, compressed water (subcritical water) for hydrolyzing fats and oils to produce mixtures of fatty acids for industrial use (Holliday, et al., 1997). This is very similar to the traditional “fat-splitting” processes currently used in industry except the ratio of water/fat in our process is about 2.5 versus a ratio of 0.6-0.8 commonly used in industrial fat splitters. One can achieve over 97% conversion of the starting vegetable oils to their component fatty acids using a dynamic flow system in about 10 minutes employing temperatures of 260-280°C. Pressures are typically low, 12 - 15 MPa, under these conditions, however the resultant fatty acid mixtures form an emulsion in the aqueous extract requiring further separation. As will be discussed later, we believe that this is an excellent candidate for employing a tandem process consisting of subcritical water reaction conditions followed by liquid- or SC-CO₂ extraction of the fatty

acids from the aqueous emulsion.

Supercritical Fluid Fractionation of Oleochemical-Derived Extracts and Reaction Products

As noted in the introduction, fractionation techniques employing supercritical fluids can be employed to further enrich a supercritical-derived extract or reaction product, or be applied to neat oils to enrich a particular desired component. With respect to the latter operation, we conducted research at NCAUR designed to win high value ingredients from vegetable oils, such as tocopherols, phospholipids, and sterols. In a previously reported study (King, et al., 1996) have shown that by careful control of SFE parameters, it is possible to produce an enrichment of tocopherol components in a soybean oil extract. This is achieved because of the differential extraction rates of tocopherols relative to the triglycerides in the oil at 25 MPa and 80°C which produces enrichment factors relative to their concentration in soybean ranging from 1.8 - 4.3. To provide further enrichment, these researchers further employed preparative scale supercritical fluid chromatography (SFC) on the extracts from the SFE stage using a commodity, low price silica gel. After screening sets of extraction conditions, further enrichment was affected by conducting SFC at 25 MPa and 40°C. After this operation was performed, enrichment factors rose from 2.5 to 31 depending on the individual tocopherol. This type of tandem enrichment process shows considerable promise for isolating high value phytochemicals from vegetable oil matrices without introducing solvent residuals into the oil matrix. Similar studies of this type are also ongoing at NCAUR utilizing SC-CO₂/ethanol cosolvent mixtures for fractionating vegetable oil-derived lecithins into their phospholipid components utilizing sequential SFE and SFC.

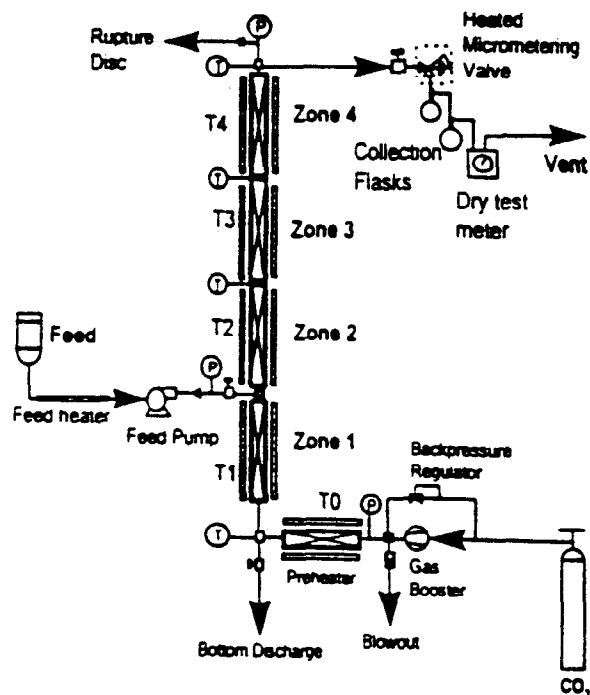


Fig. 5. Schematic of the packed column fractionation system.

Another supercritical fluid based fractionation process that is currently being used at NCAUR is the use of a thermal gradient fractionating tower for enriching monoglyceride-containing mixtures. In these studies we have used the semibatch fractionation approach of Nilsson, et al. (1988) who fractionated fish oil esters for nutraceutical use with this procedure. In our experiments (King, et al., 1997b), a packed 56 cm long column (1.43 cm in diameter) was used at pressures between 20 - 35 MPa, incorporating a thermal gradient ranging from 65 - 95°C (see Figure 5) to enrich the monoglycerides in reaction mixtures containing all glyceride species. Hence, glycerolysis products from either the CO₂ or enzyme-initiated glycerolysis can be further enriched and purified by this method. Fractionating efficiency is an acute function of glyceride throughput and pressure, the optimal fractionation occurring at lower pressures (17.5 MPa). Enrichment to monoglyceride levels between 90 - 95 wt. % is possible by this method, equal those attained by molecular distillation. It is possible therefore to envision a process whereby the raffinate in this fractionation scheme could be returned to a reaction process and be further converted to monoglycerides via a SFR.

Integrated Supercritical Fluid-Based Processing

The above examples taken from our research at NCAUR illustrate the expanding role and possibilities that supercritical fluid-based processing potentially offer the oilseeds processing and converting industry. Although the concept of an integrated SFE-SFF-SFR processing scenario may seem somewhat futuristic, it does offer the industry a range of possibilities for environmental compliance and to produce superior and value-added products from their feedstocks. As illustrated above in integrating a SFR sequence (glycerolysis using SC-CO₂) with a SFF step (fractionation of monoglycerides), there are several other tandem processes that would allow the use of sub- and supercritical fluid media to process oleochemicals. Several of these options are enumerated below:

- Ester Synthesis via SFR/Ester Fractionation by SFF
- Fatty Acid Production via SFR/Fatty Acid Isolation by SFE
- Phospholipid Isolation by SFE/Phospholipid Enrichment by SFC
- Ester Production via SFR/Ester Hydrogenation by SFR

The last option is particularly interesting since it advocates conducting hydrogenations in supercritical fluid media. Several reports (Tacke, et al., 1996; Harrod and Moller, 1996) have appeared that describe the hydrogenation of fats and oils under supercritical conditions, particularly in continuous flow reactor systems exhibiting high throughput and fast conversion efficiencies. The basis of this reported performance again lies in the superior mass transport properties exhibited by reactants in supercritical fluids, particularly the ability to enhance contact between the hydrogen, catalyst moiety, and lipid specie under these conditions. The recorded low trans content of oils hydrogenated under these conditions is encouraging, but the oilseed processing industry would have to be willing to consider retooling for this new processing option.

Impact of Analytical Supercritical Fluid Based Methodology on the Oilseed Processing Industry

Unfortunately time and space limitations limit a thorough discussion of the impact of analytical supercritical fluid methodology and its implications for the oilseed processing industry, but the author would be remiss not to mention developments in this area, including analytical research at NCAUR which have formed the basis of current developments. A nice summary of the research to date has been provided by King (1998). Utilizing SC-CO₂, it is now possible to determine the oil content of seeds using analytical SFE (Taylor, et al., 1993). Recently a collaborated method has been approved by the AOCS and it is described by King and O'Farrell (1997). Based on our previously described synthetic research, we have developed a unique and highly specific method for determining lipid levels in a variety of food matrices, including oilseeds (Snyder, et al., 1997). This automated analytical method evolved from our process studies to enzymatically convert seed oils to biodiesel in SC-CO₂ media, as depicted in Figure 6.

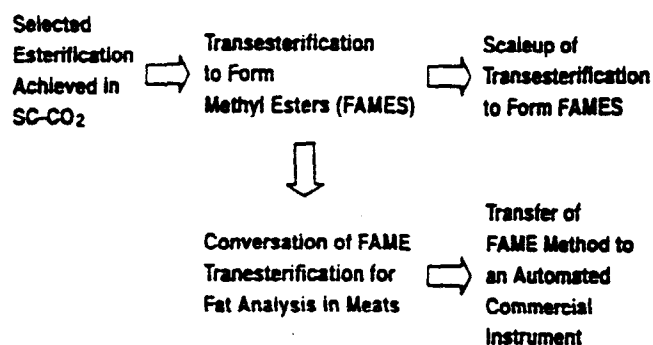


Fig. 6. Development and Utilization of Lipase Reaction in SC-CO₂.

Recently this approach has been employed to determine the total fatty acid content of commercial soapstocks (King, et al., 1998). This method is summarized in Figure 7, where the SFE/SFR-based method is compared to AOCS Official Method G3-53, a titrimetric and solvent extraction-based method. Clearly the supercritical fluid based method is quicker to perform and substantially reduces the quantity of solvent required in the laboratory environment. We further believe that the method is more accurate than the conventional method for determining the fatty acid content of soapstock (Method G3-53), since the lipid content of the soapstock is based on a rigorous gas chromatographic-fatty acid methyl ester conducted after the SFE/SFR has been performed on the soapstock sample. It is also interesting to note in Figure 7, that a capillary SFC-based method provides an approximate analysis of the fatty acid content of the soapstock in 45 minutes while using minimal solvent. This is again another example of the versatility of supercritical fluids and the promise they hold for the oilseed processing industry.

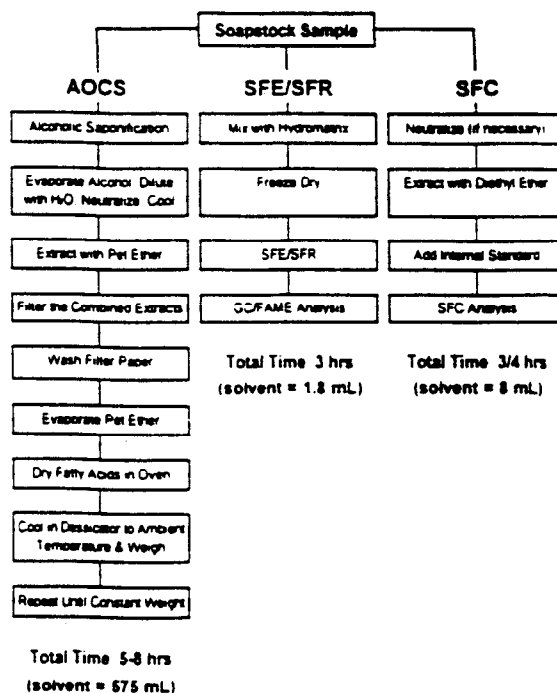


Fig. 7. Comparison of AOCS Official Method G3-53 with the SFE/SFR and SFC Methods.

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